Correlations Between $PM_{2.5}$ Mass, Aerosol Constituents (EC and SO_4^{2-}), and Their Precursors for Different Averaging Times—Source Impact Indicator?

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Summary

Quantification of the relative impacts of primary and secondary sources of $PM_{2.5}$ particles on sensitive receptor sites has been hampered by limited concurrent data for precursor gaseous species (CO, SO_2, NO, NO_2, NO_y, O_3) and meteorology, and by reliance on 24-h integrated samples for aerosol mass and its chemical constituents. Events in which sites are impacted by sources of gaseous and/or particulate pollutants for periods of much less than 24h cannot be easily or accurately reflected in reported exposures if only 12- or 24-h data are available. To address this limitation, TVA has been operating an enhanced monitoring site since 1999 at a site at Look Rock, TN, collocated with the IMPROVE network site, and just to the west of Great Smoky Mountains National Park (GSNMP). Several (usually) month-long campaigns have now been completed in various seasons at this site, during which continuous $PM_{2.5}$ mass measurements have been made with a Tapered Element Oscillating Microbalance (TEOM) with a 2.5 μm inlet, supplemented by continuous measurements of black (elemental) carbon by aethalometer, and more recently, of sulfate using two newly available instruments. Continuous trace gas and meteorological data were also taken by TVA personnel during these campaigns. These continuous data, averaged to 1-h or less time resolution, have now been compiled, and permit a more precise definition of the temporal extent and magnitude of source impacts at this site.

The enhanced monitoring (background) site at Look Rock, frequently experiences periods of short-term impact by gaseous and particulate species in all seasons, based on observations made by TVA at this site from October 1999 through November, 2001. Correlations between various aerosol species and their expected gaseous precursors are reported in this work for the Look Rock site, and suggest that actual exposure is more accurately reflected by short-time resolution data. Short-term correlations also show promise for differentiating various types of impacting sources and to differentiate local sources from regional sources whose variability reflects synoptic meteorological conditions. For example, exposures in which elevated CO, black carbon, and NO_y concentrations are highly correlated appear to reflect the influence of the nearby urban area (i.e., greater Knoxville), whereas correlated elevated SO_2 and NO_y concentrations reflect the influence of point source plumes, and the duration of the exposures reflects the transport distance from these point sources.

Our preliminary indication is that short-time-resolution fine mass as measured by the TEOM is positively correlated with CO ($r^2 \approx 0.4$) but not with SO_2. It is clear that secondary formation of sulfate occurs in (largely) point source plumes containing SO_2, but the process is sufficiently slow that SO_2 and fine mass concentrations may be decoupled. Short term variations in fine mass appear to be moderately correlated with stable primary emissions of CO, largely due to transportation sources in the region near the Look Rock site (in the range of 50-200 km distance).

Development of accurate back-trajectories for Look Rook/GSMNP locations is difficult because of the complex, mountainous terrain, and their use in identification of sources impacting the site is quite limited. For example, winds on 23 August 2000 were initially S to SSW at 0600, gradually shifting to northerly by mid-afternoon, then suddenly shifted back to SSW to SW about 1630 hours, and remained SW through the evening hours. These wind direction shifts are largely driven by upslope-down slope circulation on summer days, and are not represented in simulations of regional, synoptic circulations. The value of short-term sampling for both gases and particles (mass and concentration) are evident from the data for August 23, 2000, in which the shifting winds at the ridge-top site apparently caused successive impacts from an SO_2-rich air mass with modest CO, then an SO_2-poor air mass with higher CO, both air masses containing elevated NO_y levels.

Despite meteorological complications, the magnitude of impacts from various sources may now be determinable with higher accuracy though the use of short-time resolution measurements of fine particle mass and composition along with the gaseous precursors to the secondary components of fine particles. Recently (July, 2001) we have added short-time-resolution aerosol sulfate measurements to the suite measured at Look Rock, and an example of how this additional capability may greatly improve the parsing of contributions of urban, power plant, and natural sources to fine mass composition at this site will be given.